

Surface Engineering of Chemically Exfoliated MoS₂ in a "click": How to Generate Versatile Multifunctional Transition Metal Dichalcogenides-Based Platforms

Tuci G., Mosconi D., Rossin A., Luconi L., Agnoli S., Righetto M., Pham-Huu C., Ba H., Cicchi S., Granozzi G., Giambastiani G.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

Copyright © 2018 American Chemical Society. The interest for transition metal dichalcogenides (TMDs) as two-dimensional (2D) analogues of graphene is steadily growing along with the need of efficient and easy tunable protocols for their surface functionalization. This latter aspect holds a key role in the widespread application of TMDs in various technological fields and it represents the missing step to bridge the gap between the more popular C sp²-based networks and their inorganic counterparts. Although significant steps forward have already been made in the field of TMDs functionalization (particularly for MoS₂), a rational approach to their surface engineering for the generation of 2D organic-inorganic hybrids capable to accommodate various molecules featured by orthogonal groups has not been reported yet. The paper paves the way toward a new frontier for "click" chemistry in material science. It describes the post-synthetic modification (PSM) of covalently decorated MoS₂ nanosheets with phenylazido pendant arms and the successful application of CuAAC chemistry (copper-mediated azide-alkyne cycloaddition) towards the generation of highly homo- and hetero-decorated MoS₂ platforms. This contribution goes beyond the proof of evidence of the chemical grafting of organic groups to the surface of exfoliated MoS₂ flakes through covalent C-S bonds. It also demonstrates the versatility of the hybrid samples to undergo post-synthetic modifications thus imparting multimodality to these 2D materials. Several physico-chemical [SEM microscopy, fluorescence lifetime imaging (FLIM)], spectroscopic (IR, Raman, XPS, UV-vis), and analytical tools have been combined together for the hybrids' characterization as well as for the estimation of their functionalization loading.

<http://dx.doi.org/10.1021/acs.chemmater.8b03663>

References

- [1] Ramakrishna Matte, H. S. S.; Gomathi, A.; Manna, A. K.; Late, J. D.; Datta, R.; Pati, S. K.; Rao, C. N. R. MoS and WS analogues of graphene. *Angew. Chem., Int. Ed.* 2010, 49, 4059-4062, 10.1002/anie.201000009
- [2] Rao, C. N. R.; Ramakrishna Matte, H. S. S.; Maitra, U. Graphene analogues of inorganic layered materials. *Angew. Chem., Int. Ed.* 2013, 52, 13162-13185, 10.1002/anie.201301548
- [3] Late, D. J.; Liu, B.; Matte, H. S. S. R.; Dravid, V. P.; Rao, C. N. R. Hysteresis in Single-Layer MoS₂ Field Effect Transistors. *ACS Nano* 2012, 6, 5635-5641, 10.1021/nn301572c
- [4] Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* 2012, 7, 699-712, 10.1038/nnano.2012.193

- [5] Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutierrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; Johnston-Halperin, E.; Kuno, M.; Plashnitsa, V. V.; Robinson, R. D.; Ruoff, R. S.; Salahuddin, S.; Shan, J.; Shi, L.; Spencer, M. G.; Terrones, M.; Windl, W.; Goldberger, J. E. Progress, challenges, and opportunities in two-dimensional materials beyond graphene. *ACS Nano* 2013, 7, 2898-2926, 10.1021/nn400280c
- [6] Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* 2013, 5, 263-275, 10.1038/nchem.1589
- [7] Shi, Y.; Li, H.; Li, L.-J. Recent advances in controlled synthesis of two-dimensional transition metal dichalcogenides via vapour deposition techniques. *Chem. Soc. Rev.* 2015, 44, 2744-2756, 10.1039/C4CS00256C
- [8] Zheng, J.; Zhang, H.; Dong, S.; Liu, Y.; Nai, C. T.; Shin, H. S.; Jeong, H. Y.; Liu, B.; Loh, K. P. High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nat. Commun.* 2014, 5, 2995, 10.1038/ncomms3995
- [9] Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from chemically exfoliated MoS. *Nano Lett.* 2011, 11, 5111-5116, 10.1021/nl201874w
- [10] Anto Jeffery, A.; Nethravathi, C.; Rajamathi, M. Two-dimensional nanosheets and layered hybrids of MoS and WS through exfoliation of ammoniated MS (M = Mo, W). *J. Phys. Chem. C* 2014, 118, 1386-1396, 10.1021/jp410918c
- [11] Varrla, E.; Backes, C.; Paton, K. R.; Harvey, A.; Gholamvand, Z.; McCauley, J.; Coleman, J. N. Large-scale production of size-controlled MoS nanosheets by shear exfoliation. *Chem. Mater.* 2015, 27, 1129-1139, 10.1021/cm5044864
- [12] Nicolosi, V.; Chhowalla, M.; Kanatzidis, M. G.; Strano, M. S.; Coleman, J. N. Liquid exfoliation of layered materials. *Science* 2013, 340, 1226-1229, 10.1126/science.1226419
- [13] Presolski, S.; Pumera, M. Covalent functionalization of MoS. *Mater. Today* 2016, 19, 140-145, 10.1016/j.mattod.2015.08.019
- [14] Chen, X.; Berner, N. C.; Backes, C.; Duesberg, G. S.; McDonald, A. R. Functionalization of two-dimensional MoS: On the reaction between MoS and organic thiols. *Angew. Chem., Int. Ed.* 2016, 55, 5803-5808, 10.1002/anie.201510219
- [15] Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically thin MoS: A new direct-gap semiconductor. *Phys. Rev. Lett.* 2010, 105, 136805, 10.1103/PhysRevLett.105.136805
- [16] Tsai, H.-L.; Heising, J.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. Exfoliated-restacked phase of WS. *Chem. Mater.* 1997, 9, 879-882, 10.1021/cm960579t
- [17] Voiry, D.; Salehi, M.; Silva, R.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. Conducting MoS nanosheets as catalysts for hydrogen evolution reaction. *Nano Lett.* 2013, 13, 6222-6227, 10.1021/nl403661s
- [18] Backes, C.; Berner, N. C.; Chen, X.; Lafargue, P.; LaPlace, P.; Freeley, M.; Duesberg, G. S.; Coleman, J. N.; McDonald, A. R. Functionalization of Liquid-Exfoliated Two-Dimensional 2H-MoS. *Angew. Chem., Int. Ed.* 2015, 54, 2638-2642, 10.1002/anie.201409412
- [19] Chou, S. S.; De, M.; Kim, J.; Byun, S.; Dykstra, C.; Yu, J.; Huang, J.; Dravid, V. P. Ligand conjugation of chemically exfoliated MoS. *J. Am. Chem. Soc.* 2013, 135, 4584-4587, 10.1021/ja310929s
- [20] Zhou, L.; He, B.; Yang, Y.; He, Y. Facile approach to surface functionalized MoS nanosheets. *RSC Adv.* 2014, 4, 32570-32578, 10.1039/C4RA04682J
- [21] Kim, J.-S.; Yoo, H.-W.; Choi, H. O.; Jung, H. T. Tunable volatile organic compounds sensor by using thiolated ligand conjugation on MoS. *Nano Lett.* 2014, 14, 5941-5947, 10.1021/nl502906a
- [22] Li, B. L.; Setyawati, M. I.; Chen, L.; Xie, J.; Ariga, K.; Lim, C.-T.; Garaj, S.; Leong, D. T. Directing Assembly and Disassembly of 2D MoS₂ Nanosheets with DNA for Drug Delivery. *ACS Appl. Mater. Interfaces* 2017, 9, 15286-15296, 10.1021/acsami.7b02529
- [23] Voiry, D.; Goswami, A.; Koppera, R.; de Carvalho Castro e Silva, C.; Kaplan, D.; Fujita, T.; Chen, M.; Asefa, T.; Chhowalla, M. Covalent functionalization of monolayered transition metal dichalcogenides by phase engineering. *Nat. Chem.* 2015, 7, 45-49, 10.1038/nchem.2108
- [24] Knirsch, K. C.; Berner, N. C.; Nerl, H. C.; Cucinotta, C. S.; Gholamvand, Z.; McEvoy, N.; Wang, Z.; Abramovic, I.; Vecera, P.; Halik, M.; Sanvito, S.; Duesberg, G. S.; Nicolosi, V.; Hauke, F.; Hirsch, A.; Coleman, J. N.; Backes, C. Basal-plane functionalization of chemically exfoliated molybdenum disulfide by diazonium salts. *ACS Nano* 2015, 9, 6018-6030, 10.1021/acs.nano.5b00965
- [25] Cai, M.; Zhang, F.; Zhang, C.; Lu, C.; He, Y.; Qu, Y.; Tian, H.; Feng, X.; Zhuang, X. Cobaloxime anchored MoS nanosheets as electrocatalysts for the hydrogen evolution reaction. *J. Mater. Chem. A* 2018, 6, 138-144, 10.1039/C7TA08684A
- [26] Benson, E. E.; Zhang, H.; Schuman, S. A.; Nanayakkara, S. U.; Bronstein, N. D.; Ferrere, S.; Blackburn, J. L.; Miller, E. M. Balancing the hydrogen evolution reaction, surface energetics, and stability of metallic MoS nanosheets via covalent functionalization. *J. Am. Chem. Soc.* 2018, 140, 441-450, 10.1021/jacs.7b11242

- [27] Bottari, G.; Herranz, A.; Wibmer, L.; Volland, M.; Rodríguez-Pérez, L.; Guldi, D. M.; Hirsch, A.; Martín, N.; D'Souza, F.; Torres, T. Chemical functionalization and characterization of graphene-based materials. *Chem. Soc. Rev.* 2017, 46, 4464-4500, 10.1039/C7CS00229G
- [28] Tuci, G.; Luconi, L.; Rossin, A.; Baldini, F.; Cicchi, S.; Tombelli, S.; Trono, C.; Giannetti, A.; Manet, I.; Fedeli, S.; Brandi, A.; Giambastiani, G. A hetero-bifunctional spacer for the smart engineering of carbon-based nanostructures. *ChemPlusChem* 2015, 80, 704-714, 10.1002/cplu.201402391
- [29] Tuci, G.; Vinattieri, C.; Luconi, L.; Ceppatelli, M.; Cicchi, S.; Brandi, A.; Filippi, J.; Melucci, M.; Giambastiani, G. "Click" on tubes: A versatile approach towards multimodal functionalization of SWCNTs. *Chem.-Eur. J.* 2012, 18, 8454-8463, 10.1002/chem.201200650
- [30] Tuci, G.; Rossin, A.; Xu, X.; Ranocchiari, M.; Van Bokhoven, J. A.; Luconi, L.; Manet, I.; Melucci, M.; Giambastiani, G. "Click" on MOFs: A versatile tool for the multimodal derivatization of N-decorated metal organic frameworks. *Chem. Mater.* 2013, 25 (11), 2297-2308, 10.1021/cm400899a
- [31] Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. A stepwise Huisgen cycloaddition process: Copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes. *Angew. Chem., Int. Ed.* 2002, 41, 2596-2599, 10.1002/1521-3773(20020715)41:14<2596::AID-ANIE2596>3.0.CO;2-4
- [32] Lutz, J.-F. 1,3-dipolar cycloadditions of azides and alkynes: A universal ligation tool in polymer and materials science. *Angew. Chem., Int. Ed.* 2007, 46, 1018-1025, 10.1002/anie.200604050
- [33] Xi, W.; Scott, T. F.; Kloxin, C. J.; Bowman, C. N. Click chemistry in materials science. *Adv. Funct. Mater.* 2014, 24, 2572-2590, 10.1002/adfm.201302847
- [34] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: 1980; Vol. 1.
- [35] KolibriK.net. <https://www.kolibrik.net/kolxpd/> (accessed Nov. 10, 2018).
- [36] Zhang, A. J.; Russell, D. H.; Zhu, J.; Burgess, K. A method for removal of N-BOC protecting groups from substrates on TFA-sensitive resins. *Tetrahedron Lett.* 1998, 39, 7439-7442, 10.1016/S0040-4039(98)01631-1
- [37] Ghasemi, M.; Minier, M.; Tatoulian, M.; Arefi-Khonsari, F. Determination of amine and aldehyde surface densities: Application to the study of aged plasma treated polyethylene films. *Langmuir* 2007, 23, 11554-11561, 10.1021/la701126t
- [38] Kam, N. W. S.; Liu, Z.; Dai, H. Functionalization of carbon nanotubes via cleavable disulfide bonds for efficient intracellular delivery of siRNA and potent gene silencing. *J. Am. Chem. Soc.* 2005, 127, 12492-12493, 10.1021/ja053962k
- [39] Wang, D.; Zhang, X.; Bao, S.; Zhang, Z.; Fei, H.; Wu, Z. Phase engineering of a multiphasic 1T/2H MoS catalyst for highly efficient hydrogen evolution. *J. Mater. Chem. A* 2017, 5, 2681-2688, 10.1039/C6TA09409K
- [40] Acerce, M.; Voiry, D.; Chhowalla, M. Metallic 1T phase MoS nanosheets as supercapacitor electrode materials. *Nat. Nanotechnol.* 2015, 10, 313-318, 10.1038/nnano.2015.40
- [41] Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous lattice vibrations of single and few-layer MoS. *ACS Nano* 2010, 4, 2695-2700, 10.1021/nn1003937
- [42] Zhang, X.; Qiao, X.-F.; Shi, W.; Wu, J.-B.; Jiang, D. S.; Tan, P.-H. Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. *Chem. Soc. Rev.* 2015, 44, 2757-2785, 10.1039/C4CS00282B
- [43] Presolski, S.; Wang, L.; Loo, A. H.; Ambrosi, A.; Lazar, P.; Ranc, V.; Otyepka, M.; Zboril, R.; Tomanec, O.; Ugoletti, J.; Sofer, Z.; Pumera, M. Functional nanosheet synthons by covalent modification of transition-metal dichalcogenides. *Chem. Mater.* 2017, 29, 2066-2073, 10.1021/acs.chemmater.6b04171
- [44] Dyke, C. A.; Tour, J. M. Solvent-free functionalization of carbon nanotubes. *J. Am. Chem. Soc.* 2003, 125, 1156-1157, 10.1021/ja0289806
- [45] Bahr, J. L.; Tour, J. M. Highly functionalized carbon nanotubes using in situ generated diazonium compounds. *Chem. Mater.* 2001, 13, 3823-3824, 10.1021/cm0109903
- [46] Englert, J. M.; Dotzer, C.; Yang, G.; Schmid, M.; Papp, C.; Gottfried, J. M.; Steinruck, H.-P.; Spiecker, E.; Hauke, F.; Hirsch, A. Covalent bulk functionalization of graphene. *Nat. Chem.* 2011, 3, 279-286, 10.1038/nchem.1010
- [47] Lieber, E.; Rao, C. N. R.; Chao, T. S.; Hoffman, C. W. W. Infrared Spectra of Organic Azides. *Anal. Chem.* 1957, 29, 916-918, 10.1021/ac60126a016
- [48] Fedeli, S.; Brandi, A.; Venturini, L.; Chiarugi, P.; Giannoni, E.; Paoli, P.; Corti, D.; Giambastiani, G.; Tuci, G.; Cicchi, S. The "click-on-tube" approach for the production of efficient drug carriers based on oxidized multi-walled carbon nanotubes. *J. Mater. Chem. B* 2016, 4, 3823-3831, 10.1039/C6TB00304D
- [49] Zhu, S.; Gong, L.; Xie, J.; Gu, Z.; Zhao, Y. Design, synthesis, and surface modification of materials based on transition-metal dichalcogenides for biomedical applications. *Small Methods* 2017, 1, 1700220, 10.1002/smt.201700220
- [50] Guo, Y.; Xu, K.; Wu, C.; Zhao, J.; Xie, Y. Surface chemical-modification for engineering the intrinsic physical properties of inorganic two-dimensional nanomaterials. *Chem. Soc. Rev.* 2015, 44, 637-646, 10.1039/C4CS00302K

- [51] Chen, X.; McDonald, A. R. Functionalization of two-dimensional transition-metal dichalcogenides. *Adv. Mater.* 2016, 28, 5738-5746, 10.1002/adma.201505345
- [52] Li, Z.; Wong, S. L. Functionalization of 2D transition metal dichalcogenides for biomedical applications. *Mater. Sci. Eng., C* 2017, 70, 1095-1106, 10.1016/j.msec.2016.03.039
- [53] Hirsch, A.; Hauke, F. Post-graphene 2D chemistry: The emerging field of molybdenum disulfide and black phosphorus functionalization. *Angew. Chem., Int. Ed.* 2018, 57, 4338-4354, 10.1002/anie.201708211
- [54] Pérez-Balderas, F.; Ortega-Munoz, M.; Morales-Sanfrutos, J.; Hernández-Mateo, F.; Calvo-Flores, F. G.; Calvo-Asín, J. A.; Isac-García, J.; Santoyo-González, F. Multivalent neoglycoconjugates by regiospecific cycloaddition of alkynes and azides using organic-soluble copper catalysts. *Org. Lett.* 2003, 5, 1951-1954, 10.1021/ol034534r
- [55] Ménard-Moyon, C.; Fabbro, C.; Prato, M.; Bianco, A. One-pot triple functionalization of carbon nanotubes. *Chem.-Eur. J.* 2011, 17, 3222-3227, 10.1002/chem.201003050
- [56] Pastorin, G.; Wu, W.; Wieckowski, S.; Briand, J.-P.; Kostarelos, K.; Prato, M.; Bianco, A. Double functionalisation of carbon nanotubes for multimodal drug delivery. *Chem. Commun.* 2006, 1182-1184, 10.1039/b516309a
- [57] You, Y.-Z.; Hong, C.-Y.; Pan, C.-Y. Covalently immobilizing a biological molecule onto a carbon nanotube via a stimuli-sensitive bond. *J. Phys. Chem. C* 2007, 111, 16161-16166, 10.1021/jp073324j
- [58] Beak, P. Energies and alkylations of tautomeric heterocyclic compounds: old problems-new answers. *Acc. Chem. Res.* 1977, 10, 186-192, 10.1021/ar50113a006
- [59] Stoyanov, S.; Petkov, I.; Antonov, L.; Stoyanova, T.; Karagiannidis, P.; Aslanidis, P. Thione-thiol tautomerism and stability of 2- and 4-mercaptopyridines and 2-mercaptopyrimidines. *Can. J. Chem.* 1990, 68, 1482-1489, 10.1139/v90-227
- [60] Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. Electronic structure control of single-walled carbon nanotube functionalization. *Science* 2003, 301, 1519-1522, 10.1126/science.1087691
- [61] Salice, P.; Fabris, E.; Sartorio, C.; Fenaroli, D.; Figà, V.; Casaletto, M.-P.; Cataldo, S.; Pignataro, B.; Menna, E. An insight into the functionalisation of carbon nanotubes by diazonium chemistry: Towards a controlled decoration. *Carbon* 2014, 74, 73-82, 10.1016/j.carbon.2014.02.084
- [62] Becker, W. Fluorescence lifetime imaging-techniques and applications. *J. Microsc.* 2012, 247, 119-136, 10.1111/j.1365-2818.2012.03618.x
- [63] Li, J.; Krasavin, A. V.; Webster, L.; Segovia, P.; Zayats, A. V.; Richards, D. Spectral variation of fluorescence lifetime near single metal nanoparticles. *Sci. Rep.* 2016, 6, 21349, 10.1038/srep21349
- [64] Aute, S.; Maity, P.; Das, A.; Ghosh, H. N. Demonstrating the role of anchoring functionality in interfacial electron transfer dynamics in the newly synthesized BODIPY-TiO nanostructure composite. *New J. Chem.* 2017, 41, 5215-5224, 10.1039/C7NJ00668C
- [65] Kaiser, E.; Colese, R. L.; Bossinger, C. D.; Cook, P. I. Color test for detection of free terminal amino groups in the solid-phase synthesis of peptides. *Anal. Biochem.* 1970, 34, 595-598, 10.1016/0003-2697(70)90146-6